# Structural and Photo-Conducting Properties of $Cd_{1-x}Al_xS$ Thin Films Prepared by Spray Pyroliysis

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**Abstract.** Structural and photo conducting properties of Al doped CdS thin films prepared by a low cost spray pyrolysis deposition (SPD) technique are reported in the present paper. Microstructural investigations are carried out using X-Ray Diffraction (XRD) and Atomic Force Microscopy (AFM). Crystallite and grain size of Al doped CdS thin films decreases with Al incorporation and conductivity in dark and persistent photocurrent increases with increasing Al concentration in the CdS. Prominent features are observed at low doping level (1-2%) in high activation energy, photoconductivity, photosensitivity and relaxation time. Doping of Al in CdS develops the donor energy levels between the energy gap that assists the trapping of the charge carriers and hence the enhancement in the above mentioned properties. The increase in room temperature conductivity ($\sigma_{Dark}$) upon Al doping shows the presence of charge carriers.

## INTRODUCTION

Electrical and optical properties of semiconducting materials depend strongly on defect density created by external doping as well as their preparation and growth conditions. CdS has attracted technological interest because of its tunable lattice parameters and the energy gap by various substitutions. It is one of the best photoconducting material from the family of group II–VI compounds [1]. CdS thin films are known for their various potential applications in optoelectronic devices including thin film solar cells, photo-detectors, window glass coatings, flat panel diodes, transistors and light emitting diodes. Incorporation of $Al^{3+}$ at $Cd^{2+}$ site releases an extra electron and shows n-type conductivity. Doped CdS films can be prepared by several methods such as vacuum evaporation, pulsed laser deposition, sputtering, screen printer method, chemical bath deposition, Langmuir-Blodgett and spray pyrolysis technique. The spray pyrolysis technique is a bottom up method and is a well know nanostructured thin film preparation process with excellent features due to its low cost experimental set up, high spatial selectivity, precise control, large-scale thin film production and possibility to overcome the solubility limit. In the present study, we have carried out systematic investigation on structural and optical properties of Al doped CdS thin films prepared by spray pyrolysis technique. Al doping in Cadmium sulphide forms the donor energy level that help in the trapping of the charge carriers, which in turn is the reason behind the distinction behavior of electrical and photoconducting properties of thin films.

## EXPERIMENTAL DETAILS

Al doped CdS thin films were prepared on glass substrates at $350^0$C for Al (mol %) 0, 1, 2, 3 and 5% by spray pyrolysis technique [2]. Aqueous solution 0.1 M of cadmium chloride ($CdCl_2.H_2O$) and 0.2 M thiourea ($CH_4N_2S$) were taken as the precursor for CdS thin films. The desired Al content in the sample was achieved by varying the volumetric proportion of Cd and Al precursors as per the required ratio. The flow rate of precursor solution was maintain at 1 ml/min for 15 min deposition time. The chemical reaction involved for pure and doped CdS is as follows:

$$CdCl_2.H_2O + SC(NH_2)_2 \rightarrow CdS \downarrow + CH_2N_2 + 2HCl + H_2O \quad (1)$$

$$CdCl_2.H_2O + AlCl_3 + SC(NH_2)_2 \rightarrow CdAlS \downarrow + CH_2N_2 + 4HCl + \tfrac{1}{2}Cl_2 + \tfrac{1}{2}O_2 \quad (2)$$

## RESULTS AND DISCUSSION

X-ray diffraction (XRD) patterns of Al doped CdS thin films are shown in Fig. 1. The XRD patterns were compared with the standard JCPDS data of bulk CdS for indexing the peaks and were found to be consistent with a polycrystalline hexagonal structure. The orientations of crystals are mainly in (002) and (101) directions. The diffraction peaks (100), (002) and (101) shifted towards higher 2θ values with increase in Al incorporation which indicates a contraction in unit cell volume with increase in doping level, which shows replacement of Cd ions by Al ions. The observed variation in peaks heights and the broadening seen can be attributed to the changes in the scattering factors corresponding to Al dopant.

The decrease in crystallite size is also in line with the doping induced strain [3]. Unit cell volume decreases at first and then increases with Al incorporation. Calculated lattice parameters of pure CdS thin film are a (~ 4.147 Å) and c (~ 6.738 Å) which are slightly greater than bulk CdS lattice parameters (a ~ 4.136 Å and c ~ 6.713 Å). Mean crystallite size (D) was calculated by Debye-Scherrer formula and value turns out to be ~84 nm for CdS, which is found to reduce with Al concentration to ~44 nm. This includes a correction related to the instrumental broadening reported in our previous paper Panda et al. [4].

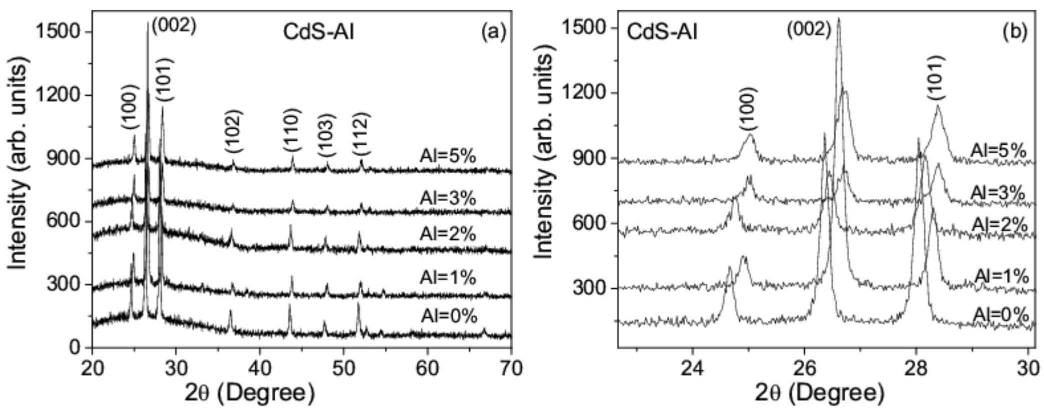


**FIGURE 1.** (a) XRD patterns of Al doped CdS thin films that show hexagonal structure of crystals in the film for Al (in mol%) is 0, 1, 2, 3, and 5%, (b) the peak shift towards higher 2θ values with Al incorporation of (100), (002) and (101) peaks.

Atomic Force Microscopy (AFM) was carried out for surface morphological studies in pure CdS thin film and it shows the rod like formation as shown in Fig. 2. It is observed that, the films incorporated with Al (mol%) 1 and 5 showed a change in the microstructure with more rounded grains [5-6]. Thin films prepared with lower concentration breaks the rods into bigger grains and these bigger grains are converted into smaller grains with increase in Al concentration due to increase of lattice strain and nano-rods morphology of CdS gets converted to broken grains morphology.

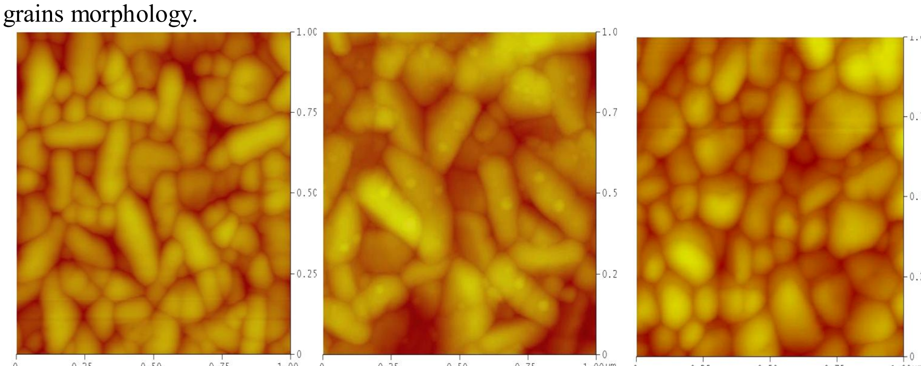

**FIGURE 2.** AFM images of $Cd_{1-x}Al_xS$ thin films for Al (mol %) 0%, 1% and 5% that shows the growth of microstructure.

Resistivity measurement was carried out by two-probe method in temperature range 200-400 K. Temperature dependence plot of resistance, corresponding to $Cd_{1-x}Al_xS$ thin films in the dark (illumination off) and light (illumination on) are shown in Fig. 3. $Cd_{1-x}Al_xS$ thin films show semiconducting behavior with temperature variation in the dark. The value of dark resistance is very high (in GΩ) as compared to the resistance in light (in MΩ). The difference between dark and light resistance at 300 K is maximum at Al doping 1-2 mol% and highest photoconductivity occur at 1 mol% doping.

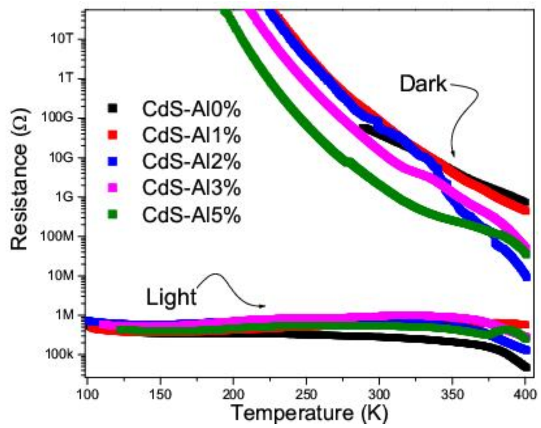


**FIGURE 3.** Variation of resistance with respect to temperature of pure and Al doped CdS thin films in dark and in light.

In the case of illumination, pure CdS film shows semiconducting behavior with temperature as shown in Fig. 4. The photoconductivity increases at initial level (1 mol%) and then decreases with further Al doping. Nevertheless, it remains higher than the pure CdS thin film. Photosensitivity of pure and Al doped CdS films also decreases with increase in temperature (210-300 K).

The dominant effect will be the trapping of photo-generated holes at the grain boundaries and the trapping of carriers in the bulk. At room temperature photocurrent is decreased from ~30 μA (for pure thin film) to ~20 μA up to 1 mol% Al doping level and reduced with further Al doping. This is due to presence of donor energy level. While electron is excited from valance band it can be trapped in the donor level. The rise in photocurrent is around 20 μA at 300K and ~23 μA at 100 K in 1 mol% Al doped film. This is changed further from ~10 μA to ~18 μA in 3 mol% Al doping. Photocurrent is less at room temperature as compared to low temperature due to decrease in mobility of charge carriers with temperature owing to the scattering from the high

## CONCLUSIONS

Al doped CdS thin films prepared by spray pyrolysis technique have been studied extensively for their photo conductive properties. Crystallite size and grain size calculated by XRD and AFM respectively decreases with Al incorporation while dislocation density, conductivity in dark and PPC effects are increased with increase in Al concentration. Al doping in CdS illustrates some special features at low doping level (1-2 mol%). These include low unit cell volume, high activation energy, high photoconductivity, high photosensitivity and high relaxation time. Al doping results rupture of rods into grains. Lattice strain increases with Al concentration which yields decrease in crystallite size and grain size. This in turn results in an enhancement of confinement effects. Substitution of $Al^{+3}$ at the place of $Cd^{+2}$ provides extra electron to the lattice that yields increase in the charge carrier concentration.

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